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Optical Absorption of Polyvinyl Alcohol Films Doped with Nickel Chloride

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Keywords- absorbance, PVA, dopand, optical band gap.

Abstract— Films of pure and doped Polyvinyl alcohol (PVA) with different concentration of Nickel Chloride (NiCl2) were prepared using the casting technique, in order to investigate the effect of NiCl2 additions on the optical properties of PVA host. The dispersion studies of pure PVA film and PVA films doped with NiCl2 were studied using complex refractive index in the wavelength range 190-1100 nm. The absorption spectral analysis showed that the optical energy band is due to the direct and indirect allowed optical transitions. The optical energy band gap E_g^{opt} of the films decreases with increasing NiCl2 contents, while the Urbach energy ΔE_t called the width of localized states in the optical band gap decreases from 0.7414 to 0.1891 eV. The reductions of optical energy band gap were observed for all samples after annealing at temperatures 70°C for three hours.

Introduction

Polymer solids have a great potential in many important applications because of their unique properties, such as low density, ability to form intricate shapes, versatile electric properties and low manufacturing cost [1]. The wide range of polymer applications can be even more extended by incorporation of filler into polymer matrix, because dispersed filler may enhance various physical properties of the host polymer [2]. The electrical and optical properties of selected polymer can be controllably modified owing to the type of the filler used, its concentration and the way in which it penetrates and interacts with the chains of the polymer [3]. Detailed studies of polymer filled with different filling levels of a certain filler allow the possibility of choice of the desired properties [4]. The use of the metal halide salts as fillers may cause modifications in the structure and consequently the physical properties of the polymer. These modifications due to filling can be attributed to the nature of the fillers as well as the method in which they interact with the polymeric host material [5].

Polyvinyl alcohol (PVA) is an interesting water-soluble synthetic polymer with a broad range of applications. The wider applications of PVA arise due to its respectable chemical and physical properties. These properties come from its hydroxyl group. The hydrogen bonding between hydroxyl groups plays an important role in determining the properties of PVA. Different additives are usually added to PVA polymer in order to modify and improve its properties and impart a high level of durability against environments. Inorganic additives such as transition metals salts have a considerable effect on the optical and electrical properties of PVA polymer [6].

The objective of present paper is to investigate the optical properties of polyvinyl alcohol (PVA) doped with varying concentration of nickel chloride (NiCl2). Different concentrations of fillers were applied in an attempt to modify the physical properties of the polymer under study and to obtain the desired filled polymer with distinct potential technological applications. The present work is mainly focused on the absorption spectrum, energy gape, and the tail of localized state of polyvinyl alcohol filled with different filling levels.

Experimental

The film of pure PVA was prepared by dissolving $2\,gm$ of Polyvinyl chloride supplied from Sigma-Aldrich Company, with $35\,ml$ of distiller water. The doping to $(5, 10\ and\ 15\,wt.\%)$ were prepared by mixing amount of $0.1, 0.2, and\ 0.3\,gm$ of nickel chloride ($NiCl_2$) into pure PVA solution, the complete dissolution was obtained using a magnetic stirrer at temperature 80^oC for $1hr$, these homogeneous solutions were spread on a glass plate. The whole assembly was placed in a dust free chamber and allowed to evaporate the solvent slowly in a dry atmosphere at temperature 35^oC, in this way; the film was prepared by isothermal evaporation technique. After 3 days the films was removed from the glass plate. The thickness of the films was in the range of $(0.19 - 0.30)mm$, it was determined using micrometer at different places in each film and an average was taken.

The optical absorption spectra of all films were recorded at room temperature, by UV-VIS double beam spectrometer (Model: Lambda 25) in the wave length range from 190 to 1100 nm. The optical band gap of these samples was evaluated from the photon energy absorption plot.

Optical Constants

Two of the most important optical properties are the refractive index n and the extinction coefficient k, which are generally called optical constants, are calculated, using the fundamental relations of photon transmittance T and absorbance A,

$$I_d = I_o e^{-\alpha d} \tag{1}$$

where I_d is the incident photon energy at thickness (d) inside the material, and I_o is incident photon energy at surface of material. The importance of the absorption coefficient is related to the valuable information that can be obtained such as the electronic band structure and the optical energy band gap [7]. Practically, the optical absorption coefficient α which is a function of wavelength can be calculated from the optical absorbance spectra by using the relation [1,8]:

$$ln\left(\frac{I_o}{I_d}\right) = \alpha d = 2.303\,A \tag{2}$$

where absorbance is defined by $A = \log(I_o/I_t)$. The reflectance (R) has been found by using the relationship:

$$R + T + A = 1 \tag{3}$$

For normal reflectance, the refractive index can be determined from the relation by:

$$n = \frac{(1+\sqrt{R})}{(1-\sqrt{R})} \tag{4}$$

The extinction coefficient is related to the absorption coefficient α by the relation [9]:

$$k = \frac{\alpha\lambda}{4\pi} \tag{5}$$

where λ is the incident photon wavelength.

Optical Band Gap

The optical band gap is the value of optical energy gap E_g^{opt} between the valance band and the conduction band. The optical band gap of the samples is determined from the absorption spectra near the absorption edges. The photon absorption in many amorphous materials is found to obey the Tauce relation [10], which is of the form:

$$\alpha(v)hv = B(hv - E_g^{opt})^m \tag{6}$$

where α is the absorption coefficient, hv is the photon energy, the factor B depends on the transition probability and can be assumed to be constant within the optical frequency range [11], and the index m is related to the distribution of the density of states. The index m has discrete values like $1/2, 3/2, 2$ or 3 depending on whether the transition is direct or indirect and allowed or forbidden, respectively [12]. The usual method for calculating E_g^{opt} is plotting $(\alpha hv)^{1/m}$ against hv, and the optical energy gap E_g^{opt} can be estimated from the extrapolation of the line portion of the graph to the photon energy axis.

The optical absorption coefficient α(v) near the band edge for many amorphous and crystalline materials, shows an exponential dependence on photon energy (hv) and obeys an empirical relation given by Urbach [13]

$$\alpha(v) = \alpha_o \exp(hv/\Delta E_t) \tag{7}$$

where α_o is a constant and ΔE_t is related to width of the band tails of localized states in the normally forbidden band gap that associated with the amorphous nature of the material. It should be mentioned that this equation is applicable only in the low absorption region ($\alpha = 10^3 - 10^4 \ cm^{-1}$).

Results and Discussion

The UV spectroscopy has been used to study the band structure and the electronic properties of pure and filled polymers. The analysis of the optical absorption spectra near the band edge lead to interesting data related to the presence of different processes occurring in polymers.

Fig. 1 displays the UV/VIS optical absorption spectra of PVA films filled with different filling levels of NiCl2. The spectrum of pure PVA is characterized by sharp absorption edge at wavelength 277nm. No absorption peaks are noticed at higher wavelengths. The sharp absorption edge at 277nm can be attributed for carbonyl groups conjugated with one ethylinic group [5]; this peak was disappeared in doped samples as shown in Fig.1b, while a new absorption peak at nearly 397nm was appeared, which may be attribute to the interaction between NiCl2 and conjugate bonds in PVA. Moreover, the figure indicates that NiCl2 enhances the UV absorption of the PVA host especially below 240 nm and at high NiCl2 content. This indicates that NiCl2 may be acts as an excellent ultraviolet shield for PVA host especially at high NiCl2 content.
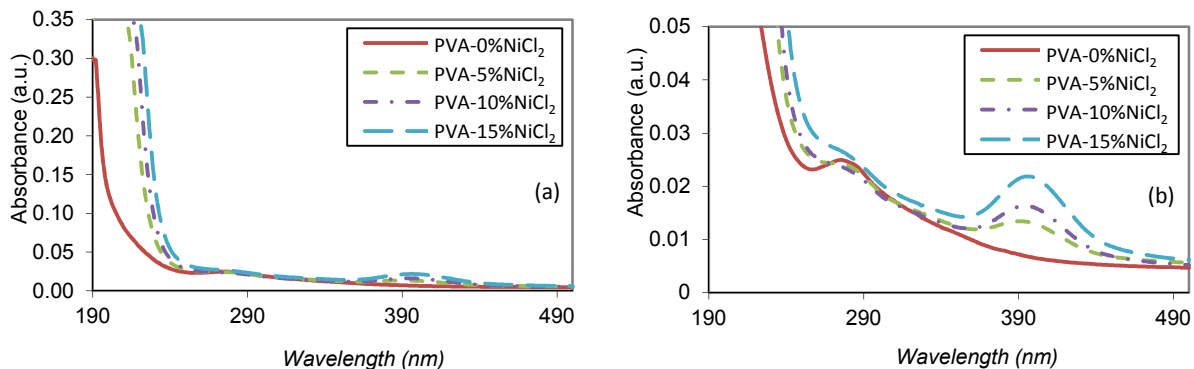

Fig. 1 The optical absorption coefficient spectrum of PVA-NiCl₂ composites.

The refractive index n over the investigated region $(190 - 500)$nm for all polymer samples are shown in Fig.2a. For the same region, the extinction coefficient K values have been calculated from a combination of reflectance and absorbance measurements at normal incidence. The variations of extinction coefficient K of all films with wavelength was shown in Fig.2b. It is clear from these figures, that the refractive index n, and extinction coefficient K are decrease with increasing wavelength; while there was an increase of refractive index values by increasing the NiCl2 content in polymer matrix, which are useful in the industry of reflectors.
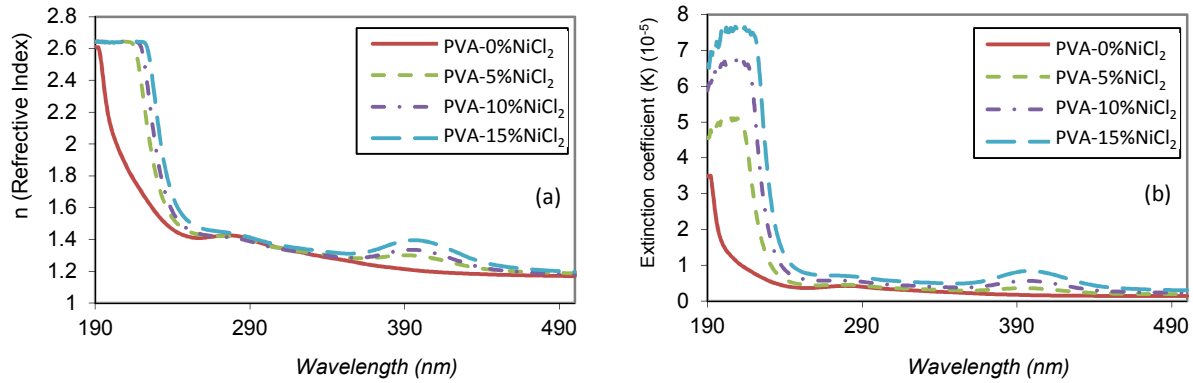
Fig.2 (a) Refractive index n, (b) Extinction coefficient K, as a function of wavelength for PVA for different NiCl$_2$ content.

By applying the equation (6) at the absorption edge, graphing the relation between photon energy (hv) versus $(\alpha hv)^{1/m}$, and extrapolating the linear part, it was found that the more linear curve was given by assuming the value of m = 1/2 and m = 2 . This indicates that the quantum selection rules allowed direct and indirect transitions [14].

The plots of $(\alpha hv)^2$, as well as $(\alpha hv)^{1/2}$ as a function of photon energy (hv) yields a good straight line fit, for direct and indirect allowed transitions respectively as shown in the Fig.3. It is to be noticed that the curves are characterized by the presence of an exponentially decaying tail at low photon energy. The optical energy gap E_g^{opt} was estimated from the extrapolation of the linear portion of the graph to the photon energy axis. It is observed that E_g^{opt} decreased with NiCl2 content, as shown in Table(1).

The optical energy gap decreases from 6.00 eV (for pure PVA) to 5.41 eV as NiCl2 concentration increases up to 15 wt%. The above results can be explained in the light of the fact that the increase in NiCl2 concentration increases the localized states within the forbidden gap. This directly affects the decrease in the optical energy gap of the PVA host [15].
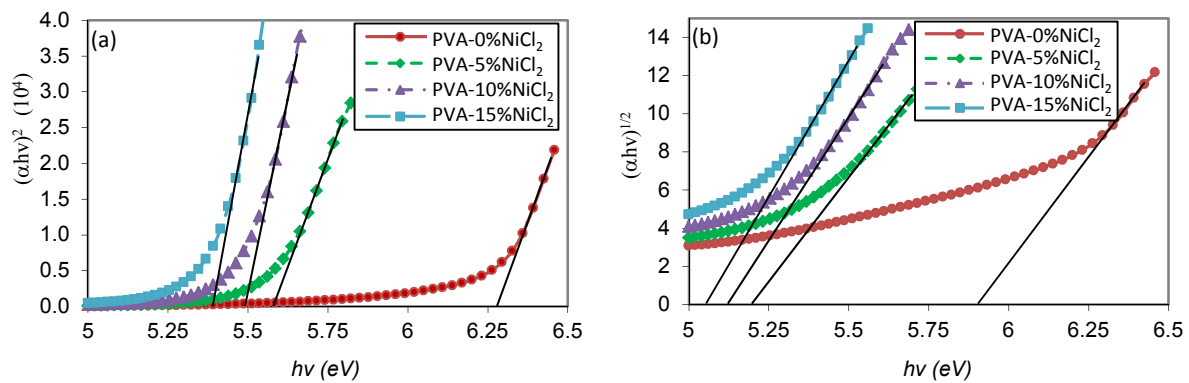

Fig.3 (a) Direct- (b) Indirect- allowed transition plot of pure and doped PVA films for different NiCl$_2$ doped concentration.

The Urbach plot is presented in Fig.4 in which the natural logarithm of absorption coefficient is plotted as a function of photon energy hv. The magnitudes of the Urbach energy ΔE_t were estimated by taking the reciprocal of the slopes of the linear portion of these curves. Noting that the origin of ΔE_t can be considered as thermal vibrations in the lattice [16]. In the present work, it seems that the dominant charge transport is through the motion of electrons for both pure and doped films, because the magnitudes of activation energies within the limits suggested by Jonscher for electronic conduction ($\leq$ 0.8 eV) [17].

Table(1): Direct, indirect optical energy gap, and band tail for PVA doped with NiCl$_2$, before and after annealing.

Samples	Before annealing			After annealing		
	Direct E_g^{opt} (eV)	Indirect E_g^{opt} (eV)	ΔE_t (eV)	Direct E_g^{opt} (eV)	Indirect E_g^{opt} (eV)	ΔE_t (eV)
$PVA - 0\%\ NiCl_2$	6.2724	5.9017	0.7416	6.2505	5.8886	0.7528
$PVA - 5\%\ NiCl_2$	5.5762	5.1926	0.2364	5.4786	5.1021	0.2584
$PVA - 10\%\ NiCl_2$	5.4844	5.1167	0.2011	5.3808	5.0263	0.2200
$PVA - 15\%\ NiCl_2$	5.3838	5.0671	0.1891	5.2816	4.9343	0.2137
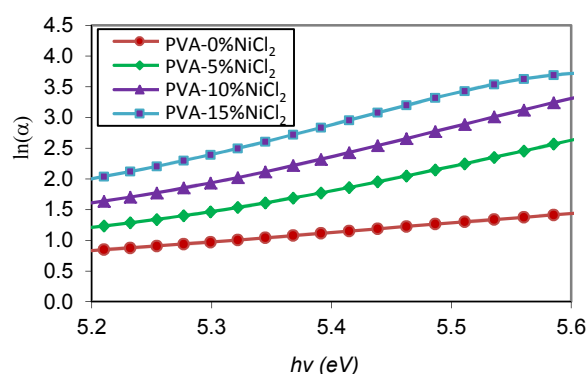
Fig.4 Relation between ln(α) and hv for pure and doped PVA films for different NiCl$_2$ concentration.

The films are thermally treated at temperature 70°C for three hours. Table (1) shows the direct and indirect allowed optical band energy gap (E_g^{opt}), and band tails of the localized state, for all samples before and after annealing. It is clearly seen that the optical energy gap for all films are decreases after annealing. The reduction of the band gap of these films after thermal treatment, and shifting the absorption properties of these organic molecules to lower energy often gives rise to stability problems to oxidation [18].

Conclusions

PVA-NiCl2 composites were prepared in order to study the effect of NiCl2 content on the optical property of PVA host. The addition of NiCl2 highly enhances the UV absorption of PVA host especially below 240 nm. The optical energy band gaps and Urbach energy tail were evaluated and their dependente on filling was investigated. Addition of NiCl2 to PVA host decreases the direct- and indirect- optical energy gap due to the increase of the localized states within forbidden gap. Moreover the redaction in optical energy gap of the samples was observed after thermal treatment.

References

[1]. V. Raja, A.K. Sarma, and V.V.R. Narasimha Rao, "Optical properties of pure and doped PMMA-CO-P4VPNO polymer films", Materials Letters 57(30), 4678-4683 (2003).

[2]. Ryo Oono, "Distribution of carbon black in SBR", Journal of Applied Polymer Science, 21(7), 1743-1749 (1977).

[3]. T. Kimura, and M. Kajiwara, "Electrical properties of poly(n-butylamino) (di-allylamino) phosphazene", Journal of Material Science, 33(11), 2955-2959 (1998).

[4]. A. El-Khodary, A.H. Oraby, and A.E. Youssef, "The effect of AgNO3 filler on the physical properties of polystyrene films", International J. of Mat. Sci. 3 (1), 11-24 (2008).

[5]. A. El-Khodary, "Vibrational, thermal, optical and magnetic investigations of PVA films filled with FeCl3 and CoCl2", Physica B 404, 1287-1294 (2009).

[6]. H. Zahr El-Deen, and A.I. Hafez, "Physico-chemical stability of PVA films doped with Mn2+ ions against weathering conditions", The Arab Journal for Science and Engineering 34 (1A), 13-26 (2009).

[7]. A. El-Khodary, "Evolution of the optical, magnetic and morphological properties of PVA films filled with CuSO4", Physica B: Condensed Matter 405 (16), 3401-3408 (2010).

[8]. J. Ballato, and S. Foulger, "Optical Properties of Perfluorocyclobutyl Polymers", Journal of Optical Society of America B 20(9), 1838-1843 (2003).

[9]. F.I. Ezema, P.U. Asogwa, A.B.C. Ekwealor, P.E. Ugwuoke, and R.U. Osuji, "Growth and optical properties of Ag2S thin films deposited by chemical bath deposition technique", Journal of the University of Chemical Technology and Metallurgy 42 (2), 217-222 (2007).

[10]. J. Tauc, A. Menth, and D. Wood, "Optical and Magnetic Investigation of the Localized States in Semiconducting Glasses", Phys. Rev. Lett. 25, 749 (1970).

[11]. D. Dorranian, Z. Abedini, A. Hojabri, M. Ghoranneviss, "Structural and optical characterization of PMMA surface treated in low power nitrogen and oxygen rf plasmas",Journal of Non-Oxide Glasses 1(3), 217-229 (2009).

[12]. F.M. Reicha, M. Ishra, and M.M. Gabr, "On the physical and electrical properties of poly propenal prepared by electropolymerization technique", J. of Phys. and Chem. of Sol. 64, 1157-1161 (2003).

[13]. F. Urbach, "The long-wavelength edge of photographic sensitivity and of the electronic absorption of solids", Phys. Rev. 92, 1324 (1953).

[14]. R.M. Ahmed "Optical study on poly(methyl methacrylate)/poly(vinyl acetate) blends", International Journal of Photoenergy 2009,1-7 (2009).

[15]. Ayman S. Ayesh, "Electrical and optical characterization of PMMA doped with Y0.0025Si0.025 Ba0.9725(Ti(0.9)Sn0.1)O3 ceramic", Chinese Journal of Polymer Science 28(4), 537-546 (2010).

[16]. A. El-Khodary, "Evolution of the optical, magnetic and morphological properties of PVA films filled with CuSO4", Physica B: Condensed Matter, 405 (16), 4301-4308 (2010).

[17]. C. Uma Devi, A.K. Sharma, and V.V.R.N. Rao, "Electrical and optical properties of pure and silver nitrate-doped polyvinyl alcohol films", Material Letters 56, 167-174 (2002).

[18]. C. Edder, P. B. Armstrong, K. B. Prado, and M.J. Fréchet, "Benzothiadiazole- and pyrrole-based polymers bearing thermally cleavable solubilizing groups as precursors for low bandgap polymers", Chem. Com. 18, 1965-1967 (2006).

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DOI References

[12] F.M. Reicha, M. Ishra, and M.M. Gabr, On the physical and electrical properties of poly propenal prepared by electropolymerization technique, J. of Phys. and Chem. of Sol. 64, 1157- 1161 (2003). http://dx.doi.org/10.1016/S0022-3697(03)00044-1